

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Resilient Stable Polyurethanes and method of making same

We, THE GENERAL TIRE & RUBBER COMPANY, a corporation organized under the laws of the State of Ohio, United States of America, of No. 1708 Englewood Avenue, 5 Akron, County of Summit, State of Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for the preparation of rubbery polyurethane foamed products from the reaction 15 between polyalkylene ether glycols and certain organic polyisocyanates, namely, those containing at least a certain proportion of a phenylene diisocyanate. In the past, polyester-diisocyanate foams have been made by reacting a non-linear slightly branched polyester with a diisocyanate and a small amount of water or by reacting a linear polyester with a mixture of di- and tri-isocyanates and water. An excess of diisocyanate over that 20 needed to react with the polyester to form the polyurethane was used to react with the water and produce carbon dioxide for forming the cells in the solid product.

The diisocyanate, therefore, was added 30 both to build up the polyester to a high molecular weight and also to crosslink the polyester sufficiently and to provide the excess carbon dioxide. Linear polymers alone did not generally change from the liquid 35 state to the solid state quickly enough to trap the CO₂ gases evolved and thereby form a desirable foamed product. Therefore, a branching material was necessary to trap and hold gaseous carbon dioxide in order to obtain a low density cellular foamed polyurethane product.

Polyethers have advantages over polyesters in their resistance to hydrolysis and in their resilient properties. Polyethers have 45 also been proposed to replace polyesters in forming the spongy materials. However, when

an attempt was made to substitute polyethers for polyesters in making foam, the proper cell structure for useable foam was not obtained; much of the carbon dioxide was lost and not entrapped even though many variations in polyethers were made. Also the curing rate of polyurethanes was generally too slow, their compression set too high, their stability was not as great as desired and their deflection-compression loading curves did not closely enough resemble those of natural rubber latex foamed materials. Foams which are more resilient and more hydrolytically stable and which have other desirable properties are in great demand.

It has been found that an improved polyetherurethane foam may be provided by reacting one mole equivalent weight of a hydroxy terminated polyalkylene ether glycol having a molecular weight of 750 to 10,000 with 1.1 to 12 mole equivalent weights of an organic polyisocyanate having at least 10% of its weight of a phenylene diisocyanate (preferably meta or para phenylene diisocyanate) in which the isocyanate groups are attached to an unsubstituted phenylene nucleus to form a moisture-free liquid "prepolymer" (as hereinafter defined) mixture containing free isocyanate groups which have not reacted with hydroxyl terminal groups of the glycol. The prepolymer subsequently is reacted by the addition of water, a polyurethane reaction catalyst, and optionally a crosslinking agent containing a plurality of labile hydrogens to the previously mentioned dry "prepolymer" forming the desired spongy polyurethane by permitting the reaction to occur in the presence of some agitation and in the presence of a silicone oil (consisting of silicon, oxygen, carbon and hydrogen atoms) so as to entrap the CO₂.

The presence of substantial quantities of one or more silicone oils is essential to the preparation of commercially acceptable polyether-urethane foams. We have been unable to obtain much blow let alone control cell

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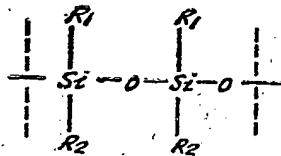
size or obtain a uniform pore size without using substantial amounts of a silicone oil as hereinafter more fully described.

We have found that polyether urethanes require relatively large amounts of silicone oil (compared with the amounts which have been used in making polyester-urethane foams), i.e., at least 0.1% of the weight of the polymer of polyether and isocyanate to increase stability of the polyethermethane and 0.25% to 1% is even better. While extremely small amounts of silicone oils have been incorporated in polyester urethanes, the effect there is quite different as silicone oil acts only to control pore size. Further, polyester urethane foams may be produced without any of the silicone oil. The amounts used in polyester-urethane foams are around 0.01% or even less and the polyester foams are extremely and adversely sensitive to substantial amounts of silicone oil.

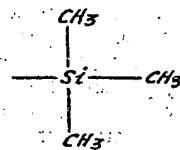
When apparatus previously used for making polyether urethane foam is used for making polyester urethane foam without solvent cleaning the apparatus the foam has substantially collapsed showing that the effect of silicone oil in polyester urethane is not stabilizing but rather defoaming. In polyether foams the effect of large amounts of silicone oil is surprisingly opposite, the effect being to stabilize the polyether-urethane foam and to permit the formation of an article of low-density.

Silicone oils that markedly improve the cell structure of polyether-urethane foams are polyorgano siloxanes such as liquid polyalkyl siloxanes including polydimethyl and polydiethyl siloxanes, polydipropyl siloxanes, and liquid polyaryl siloxanes including polydiphenyl siloxanes or mixed polyarylalkyl siloxanes such as polymethylphenyl siloxanes or liquid mixtures of one or more of such siloxanes.

In accordance with the above, oily siloxane polymers having recurring units of the following structure are useful in the present invention:



where R_1 and R_2 are hydrocarbon radicals having 1 to 6 carbon atoms such as methyl, ethyl, propyl, butyl, isopropyl, hexyl, and phenyl. R_1 and R_2 may be the same radical or different radicals. The siloxane polymers are generally terminated with a



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group although part or all of the methyl groups may be substituted for by other alkyl groups such as ethyl and propyl or an aryl radical such as phenyl. The terminal groups in the preparation of dimethyl siloxane polymers are the $-Si(CH_3)_3$ groups.

For best results of uniformity of pore size, the silicone oil should be polydimethyl siloxane. One particularly effective silicone oil is "Dow Corning 200 Fluid"—silicone oil which is a liquid, water white dimethyl siloxane polymer generally having a viscosity of about 50 centistokes at 25° C. and a pour point of -67° F. (ASTM D-97-39 Sections 5 to 7). Another very effective silicone oil is General Electric SF 96 (100) silicone fluid which is a dimethyl siloxane polymer having a viscosity at 100° F. of 100 centistokes, a pour point of -53° F. and a specific gravity (20/20° C.) of 0.965.

The viscosity of the siloxane polymer used is of importance. The lower viscosity silicone oils are more effective and may be used in smaller amounts to obtain the effects of larger amounts of the higher viscosity silicone oils. Whatever the reason for the outstanding results obtained, generally we have found that silicone oils having a viscosity range of 50 to 500 centistokes at 25° C. provide the resultant foams with the best cell structure as well as other valuable properties when used in the lower range above specified. We most frequently use silicone oils of 50 to 300 centistokes viscosity. Generally those siloxane polymers having a low viscosity less than 10 centistokes at 25° C. are undesirable.

Even though larger amounts of silicone oils are required for the higher viscosity oils, difficulty in mixing is had with viscosities above 1000 centistokes at 25° C. Apparently these more viscous siloxane polymers cannot be sufficiently dispersed unless used with some solvent to operate as effective pore size controllers. Small amounts of solvent, on the other hand may create foaming difficulties because of their high vapor pressure.

Again even though different amounts of silicone oils of different viscosities are preferably used, as low as 0.1% of any provides a noticeable improvement in stability, although 0.25% may be regarded as the minimum to give the polymethane of the invention, and as much as 5 percent by weight

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based on the weight of the prepolymer has been used. The maximum amount is determined by economy. 0.5 to 1 percent provides the resultant foam with the excellent cell structure, and is generally preferred.

It has heretofore been suggested to use in making polyurethane solid elastomers, linear prepolymers made by reacting polyether glycols with part of the diisocyanate needed to form the elastomer. However, in this prior proposal there was specified the presence during the formation of the elastomer of a small amount of an acid, i.e., a substance such as benzoyl chloride or phosphorous pentachloride or the like free of carboxyl groups so as to prevent formation of carbon dioxide. The final reaction of the prepolymer was had by adding water and agitating as in a dough mixer which would insure loss of any CO₂ formed and therefore obtain a solid rubbery mass. The not-carboxylic acid substance was required heretofore to prevent or decrease undesirable CO₂ formation. The reaction of the prepolymer with water was in the absence of any trifunctional agent which could cause growth of a three dimensional polymer. In the prior proposed process the amount of water added is large thus forming a large number of urea linkages which can then react with the diisocyanate to form biuret linkages which are relatively unstable; we have found superior results are obtained with relatively small amounts of water thus forming fewer urea crosslinkages and this tends to improve hydrolytic stability. Improved polyether-urethane foamed products have now been obtained by the intermediate formation of a moisture-free "prepolymer" formed so as to contain some free NCO groups and probably some unreacted phenylene diisocyanates as well.

Surprisingly, we have also found that the selection of a particular type of diisocyanate makes a profound difference in properties of the polyether foams. By using phenylene diisocyanates (preferably meta or para phenylene diisocyanates or mixtures thereof) as at least a 10% part of the diisocyanate by weight, an improved foamed product may be obtained. The hydrolytic stability of this product is exceptional, the resiliency is excellent and the loading curves closely resemble those of the highly regarded latex foams.

Even a relatively small amount of meta or para phenylene diisocyanate or mixtures thereof used as part of the total polyisocyanate, say 5 percent by weight, impart some benefits to the resultant foamed products. The foams cure faster to a lower compression set value and they are much more resilient and hydrolytically stable. In addition, the foams are of a lower density than when none of the phenylene diisocyanates are used which is very desirable for cushion-

ing material. The hydrolytic stability and compression set values are particularly much improved when the amount of phenylene diisocyanate is 10 percent by weight of the total polyisocyanate used. However, for most commercial uses, 20 percent by weight of phenylene diisocyanates are preferred, the density being relatively low. The humidity aging and 25 percent compression deflection properties are as well as other valuable properties also improved over those foamed materials made with a lower amount of phenylene diisocyanates, say 5 percent, in the polyisocyanate mixture.

The best results are obtained when at least 50 percent of the total diisocyanate employed in the prepolymer is a phenylene diisocyanate as evidenced by substantial improvement in some of the physical properties such as compression set. Actually, the compression set values of the foamed materials reach their lowest values when all the polyisocyanate used is a phenylene diisocyanate. However, for reasons of economy, it may be preferred to keep the proportion of phenylene diisocyanate below this aforementioned figure of 50%. As will appear from certain of the examples excellent results can still be achieved provided that at least 10% by weight of the total polyisocyanate used is a phenylene diisocyanate.

The polyether glycol used as a raw material in the present invention may, if reasonably dry, be used as commercially available or preferably may be pretreated by heating to about 100° C under a vacuum to eliminate any substantial amounts of water. The polyether glycol which should have a molecular weight above 750 may be dried by any suitable means if the water content is substantial.

The polyalkylene ether glycols have the general formula HO—(RO)_n—H, where R represents divalent aliphatic radicals such as ethylene, propylene, butylene, isopropylene, isobutylene, or tetramethylene, or aromatic hydrocarbon radicals such as phenylene, and the aliphatic or aromatic radicals may be the same or different. The integer represented by n is such that the average molecular weight of the polyether glycol is 750 to 10,000. In accordance with the present invention, greater benefits are obtained when the molecular weight is at least 900 although the best physical properties in the resultant cellular polyether urethanes are obtained when the molecular weight of the polyether glycol is 1500 to 5000, although improved products could be obtained when the molecular weight of the polyether glycol is as high as 10,000.

These polyether glycols, as well known, may be prepared by the polymerization or copolymerization of compounds like ethylene oxide, propylene oxide, butylene oxides, tetrahydrofuran, styrene oxide, epichlorohydrin, and substituted oxetanes, and are generally

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available commercially.

Among bifunctional isocyanates which may be used as the balance of the total polyisocyanate used are hexamethylene diisocyanate; 5 2,4-toluene diisocyanate; or 2,6-toluene diisocyanate; and mixtures of any of these diisocyanates.

In the preparation of these foams an equivalent weight of polyalkylene ether glycol is first reacted with from 1.1 to 1.2 equivalents, 10 and preferably from 2 to 6 equivalents of an organic polyisocyanate mixture containing the required amount of phenylene diisocyanate (preferably in an amount of at least 25 percent by weight) which preferably has 2 reactive isocyanate groups to provide a higher molecular weight polyurethane containing some free NCO groups. Some unreacted polyisocyanate may also be present. This product hereafter will be referred to as a "prepolymer".

This prepolymer is then mixed with a small amount of water, a catalyst and optionally a crosslinking compound containing a plurality of active hydrogens. The crosslinking agent preferably, when the prepolymer is formed of wholly bifunctional reactants, comprises a 25 polyfunctional material, i.e., a compound having at least 3 active hydrogen atoms, to entrap CO₂. Thorough mixing of these ingredients gives rise to a flexible foam which provides high resiliency along with good humidity aging properties.

As representative of crosslinking compounds containing a plurality of active hydrogens, we include organic polyols, such as trimethylol propane; glycerol; 1,2,4-butanetriol; hexanetriol; pentaerythritol, "Triol 230", which is the beta ethanol ether 30 of 2-methyl-, 2 methylol-, 4 methyl-, 5 hydroxy pentane; "Quadrol", which is N,N, N',N'-tetrakis (2-hydroxypropyl) ethylenediamine; and polyamines such as triamines and tetramines including hexamethylene 35 tetramine. The above crosslinking agents contain 3 to 4 active hydrogen atoms which are preferred in order to obtain the best physical properties in the resultant foamed materials.

50 A crosslinking agent is preferably but not necessarily present to obtain some processing advantages. When present, the crosslinking agent is preferably incorporated in association with the catalyst and water. The amounts of crosslinking agent used may be varied widely depending on the stiffness of the sponge desired. When less than 0.5 parts per 100 parts by weight of organic reactants (polyether plus isocyanate) is used, the 55 foamed material is often too soft or insufficiently cured for most purposes. Usually 1% to 6% of the total of polyether and isocyanate present is used, and up to 10% is sometimes used in some less flexible type foams.

60 65 When silicone oil is present in the quanti-

ties called for by this specification, a crosslinking agent surprisingly is not necessary. However, larger amounts of catalyst are then required to obtain the same properties in the foam.

The amount of water used in accordance with the present invention is dependent to some extent on the characteristics of the foam desired. We have found that the amount of water used preferably should be 0.7% to 1.5% of the weight of the prepolymer although as little as 0.5%, and as much as 5% may be used in some instances. More than 5.0% of water causes excessive formation of polyurea linkages.

As representative catalysts for the diisocyanate-polyether reaction, there are tertiary amines, such for example as di(ethyl amino ethanol) adipate. Other suitable tertiary amines are amino alcohols such as dibutyl amino ethanol, butyl diethanol amine; ordinary alkyl tertiary amines such as triethyl amine; trihexylamine, tributyl amine, or tripropyl amine; morpholines, such as N-methyl morpholine or N-octyl morpholine, pyridine compounds such as 4-pyridine propanol and 4-n-amyl pyridine. Organo metallic compounds such as cobalt and nickel naphthenates and linoleates, are also useful catalysts. Generally alkyl tertiary amines give faster acceleration than amino alcohols or morpholines or pyridines. Mixtures of alkyl tertiary amines with either morpholines or amino alcohols or pyridine compounds are preferred to give a slower acceleration. However, in some cases, especially when the amount of crosslinking agent is increased, the tri-alkyl tertiary amines alone produce excellent cellular products. The amount of catalyst used is generally .5% to 2% of the weight of the prepolymer although as little as 0.1% may be used. When the amount of the catalyst is less than 0.5% the reaction is generally too slow for economy and when much more than 4% of the catalyst is used, waste of catalyst and deterioration in quality results.

In preparing the dry prepolymer, the materials may be reacted in stages to provide known blocks (block polymerization) for example, by first reacting a mole of polyalkylene ether glycol with a large excess preferably two moles of organic diisocyanate or vice versa. Then after this reaction, the prepolymer may be further built up by adding two moles of the desired glycol, then after this reaction, reacting two moles of desired isocyanate adding alternately further glycol and isocyanate residues if required to form block polymers having the same or different isocyanate residues and glycol residues in the polymer chain. In this manner a long prepolymer chain of controlled composition is obtained. The molar ratio of glycol to diisocyanate should be held accurately for absolute control of composition but variations may be

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made while still obtaining essential control. A different polyisocyanate may be added as above indicated to change the character of the material or give a different coupling unit whenever desired. The total polyisocyanate in this liquid prepolymer should comprise at least 10 percent phenylene diisocyanate as previously discussed. The highly viscous block prepolymer, preferably prepared as above described, is mixed with excess polyisocyanate as necessary to bring the total molecular ratio of glycol to isocyanate up to between 1 to 1.1 and 1 to 1.2 as required. This block prepolymer may also be mixed with one or more lower molecular weight polyurethane prepolymers prepared when the isocyanate is in substantial molar excess over the glycol to radically change the characteristics of the building blocks of the polyurethane chain of the sponge prepared from the prepolymer. Also the usual non block prepolymer may be used alone. Thus, properties of the foamed materials may be predesigned and changed so as to alter the properties of the final product such as resiliency and flexibility at low temperatures.

The viscosity of the prepolymer may range from 1500 cps. (Brookfield) at 25° C. up to 100,000 cps. (25° C.) depending upon the types of polyether glycols and polyisocyanates used as well as their amounts with relation to each other. Higher viscosity prepolymers may require heating to 150° F. or thereabouts to

permit better flow characteristics while pumping to the mixing machine.

When the pH of the polyether glycol is alkaline, the use of acid chlorides in the prepolymer to deter premature gelling may be desirable as described in Patent Specification No. 731,071 (E. I. Du Pont de Nemours and Company).

Example I below is given by way of comparison, and the rest of the examples are used to illustrate the invention and not to limit it in any way.

EXAMPLE I

A prepolymer was prepared by reacting 600 parts by weight of "Ucon 75 H 1400" (a mixed polyethylene propylene ether glycol from Carbide and Carbon with an average molecular weight of 2500, "Ucon" being a Registered Trade Mark) with 180 parts of a 65/35 mixture of 2,4 and 2,6-toluylene diisocyanates.

The two reactants are mixed at room temperature which gives rise to a slight exotherm. When the temperature of the mixture levels off, the heat is turned on so that the batch temperature will reach approximately 100° C. in a period of one hour. The batch is then maintained at this temperature for an additional hour, followed by cooling. The prepolymer thus obtained is a viscous but pourable liquid at room temperature and is used to produce a foamed polyurethane rubber sponge using the following formula:

130	parts of prepolymer
5	parts of Quadrol (N,N,N',N'-tetrakis (2-hydroxypropyl) ethylene diamine)
1.3	parts water
1	part Silicone oil Dow Corning—200 Fluid
1.5	parts N-methyl morpholine

The Silicone oil helps in improving cell structure and is first dispersed in the prepolymer. The Quadrol, water and N-methyl morpholine were first mixed together, the prepolymer plus Silicone oil was then mixed with these ingredients and the whole poured into a mold and allowed to rise to full height. The raised foam was cured overnight at 100° C.

Foam density was slightly over 6 lbs. per cubic foot. It was passed through squeeze

rolls with just enough spacing to allow the sponge to pass therethrough without tearing it so as to rupture cell walls. After 24 passes the rebound was 37 percent as determined by the Schopper Rebound Tester. Compression deflection (25%) using a 10 sq. in. foot was 12 pounds. Compression set (ASTM method B) was 6.7 percent.

EXAMPLE II

A prepolymer was prepared as in Example I using the formula below:

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Parts by Weight	Ingredients
500 parts	Polypropylene ether glycol (M.W. about 1850)
185 parts	Para-phenylene diisocyanate
10 parts	Trinonylphenyl phosphite

The trinonylphenyl phosphite was first mixed in with the glycol and this solution heated to 145° F. The trinonyl phenyl phosphite is used to stabilize the foamed products particularly against dry aging and weathering. The p-phenylene diisocyanate, being solid at room temperature, was then heated to above its melting point, and added to the glycol with stirring. The temperature was then maintained at 60—80° C. for 2 hours, followed by 1 hour at 95° C. The resultant prepolymer was then cooled down to room temperature and its percent isocyanate and viscosity determined as follows:

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% NCO 7.7
 Viscosity (Brookfield) 10,000 cps. 23° C.

The prepolymer was further processed according to the following formula:

Parts by Weight	Ingredients
75	Prepolymer
0.7	Silicone oil
1	N-methyl morpholine
2	Water

20 The silicone oil was first dispersed in the prepolymer. The tertiary amine catalyst and water were then added and mixed into the prepolymer with rapid stirring. The foamed material rose rapidly and gave a relatively tack free surface in a matter of minutes. Tests were conducted on the foamed material, the results of which are indicated below:

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Density	3.8 lbs./cu. ft.
Schopper Rebound	53
25% Compression Deflection	0.6 lbs./sq. in.
Compression Set	3.8%

30 The percent change in 25% Deflection after 70 days exposure at 158° F. and 95—100% relative humidity was only plus 2.0%. Another prepolymer was prepared according to the formula below:

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600 parts	Polypropylene ether glycol
54 parts	Para-phenylene diisocyanate
180 parts	80/20—2,4/2,6 toluene diisocyanate

The glycol was heated to 95° C. and molten p-phenylene diisocyanate at a temperature of 95° C. was added with stirring. The mixture was then maintained at this temperature for 5 a period of 1 hour. The 80/20 mixture of 2,4- and 2,6-toluene diisocyanates was then added at this temperature and the batch was further reacted at 95–100° C. for an additional hour. The resultant prepolymer was 10 then cooled to room temperature and certain properties determined as indicated below:

%NCO	9.8
Viscosity	4,000 cps. 25° C.
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% Schopper Rebound	46
25% Compression Deflection	0.62-lb./sq. in.
Density	3.1 lbs./cu. ft.
Compression Set	12.4 %

The percent change in 25% Deflection after 14 weeks exposure in a circulating air oven at 158° F. was found to be only –2.0%.

The prepolymer was further processed in a manner similar to that described in Example I according to the following formula:

75 parts above prepolymer	15
0.3 parts silicone oil	
1 part N-methyl morpholine	20
0.5 part triethylamine	
1.5 parts water	

The properties of the resultant foamed material were determined as indicated below:

EXAMPLE IV

A prepolymer was prepared using the formula as follows:

- a. { 300 parts polypropylene ether glycol (M.W. 2000)
48 parts meta phenylene diisocyanate
- b. 600 parts polypropylene ether glycol
- c. 48 parts meta phenylene diisocyanate
- d. 260 parts TDI: (80/20) mixture of 2,4- and 2,6-toluene diisocyanate

The glycol and m-phenylene diisocyanate mixture (a) was heated to 100° C. and reacted together at this temperature for 1 hour. The second portion of glycol (b) was then added and the mixture again reacted for 1 more hour. Then, the m-phenylene diisocyanate (c) was added and the mixture was 35 maintained another hour at 100° C. Finally the TDI (d) was added and the mixture was stirred while it was cooling to room temperature.

The prepolymer was made into foamed

polyurethane material as described in Example I using the formula as follows:

75 parts above prepolymer	45
0.5 parts silicone oil	
1.0 part triethylamine	
1.5 parts water	50

The resultant foamed material was tested for certain properties, the results of which are shown below:

Density	3.0 lbs./cu. ft.
25% deflection	0.5 lbs./sq. in.
Compression set	9.0%

The percent change in deflection after exposure to an atmosphere having a relative humidity of 95—100% and a temperature of 158° F. for 35 days was —7.1%.

EXAMPLE V

A prepolymer was formed as previously described using the formula as follows:

2000 parts polypropylene ether glycol
200 parts meta phenylene diisocyanate

Above materials were combined and reacted at 60° C. for one hour. Temperature was then raised to 100° C. and reaction maintained there for one more hour. On cool-

ing, the product had an NCO content of 1.56. 360 parts of 80/20 TDI was then added and mixed in for $\frac{1}{2}$ hour. The resultant prepolymer material had a viscosity of 3870 cps. 25° C. and a % NCO value of 8.5.

The prepolymer was further processed to obtain a foamed polyurethane material using a formula as follows:

75 parts above prepolymer
0.4 parts silicone oil
0.5 parts triethylamine
2.0 parts water

The resultant foamed material was tested for certain properties as shown below:

Density	2.85 lbs./cu. ft.
% Schopper Rebound	48
25% compression deflection	0.3 lb./sq. in.
% Compression set	7.7

While polyether foamed materials with the lowest percent of compression set and the fastest curing ability may be obtained when all the polyisocyanate used is meta and para phenylene diisocyanates, it can be seen from Examples III, IV and V that excellent foamed materials can be obtained by using mixtures of phenylene diisocyanates with other polyisocyanates providing the total polyisocyanate used is at least 10 percent phenylene diisocyanates.

When such polyisocyanate mixtures are used, most of the benefits of the use of 100% phenylene diisocyanate may be obtained including resistance to degradation by high humidity at temperatures appreciably above room temperature such as, say, 140° F. to 180° F.

Dry polyalkylene ether glycols may also be pre-acted with organic triisocyanates to form a dry "prepolymer" as long as phenylene diisocyanates comprise a part of the total polyisocyanate mixture used as previously described. This "prepolymer", then, in accordance with this invention, when subsequently reacted with water and also optionally organic diols or other crosslinking compound also produces excellent resilient and humidity aging resistant polyurethane foamed materials.

The silicone oils may also be dispersed in water to provide a stable emulsion and subsequently combined with amine catalysts and additional water, if necessary. The silicones in this form may thus be introduced through the catalyst component so that prior dispersion of the silicone oils in the prepolymer

may be avoided.

WHAT WE CLAIM IS:—

1. A process for the production of a cellular elastic polyurethane, which comprises reacting one mole equivalent weight of a hydroxy terminated polyalkylene ether glycol having a molecular weight of 750 to 10,000 with 1.1 to 12 mole equivalent weights of an organic polyisocyanate having at least 10% of its weight of a phenylene diisocyanate in which the isocyanate groups are attached to an unsubstituted phenylene nucleus to form a moisture-free liquid prepolymer (as herein defined) mixture containing free isocyanate groups which have not reacted with hydroxyl terminal groups of the glycol, and reacting said prepolymer mixture with 0.5 to 5% by weight of water based on the weight of the mixture, and 0.1 to 4% by weight based on the weight of said prepolymer mixture of a polyurethane reaction catalyst in the presence of 0.25 to 5% by weight based on the weight of said prepolymer mixture of a silicone oil having a viscosity of 10 to 1,000 centistokes at 25° C. and consisting of silicon, oxygen, carbon and hydrogen atoms, to obtain a flexible cellular polyurethane reaction product.

2. A process for the production of a cellular elastic polyurethane, which comprises (A) forming a moisture-free liquid prepolymer (as herein defined) mixture by (1) reacting a hydroxy terminated polyalkylene ether glycol having a molecular weight of 750 to 10,000 with an organic polyisocyanate in an amount at least sufficient to provide a polyetherurethane having terminal isocyanato groups (2) reacting said polyetherurethane with addi-

tional glycol having a molecular weight of 750 to 10,000 in an amount sufficient to provide a polyetherurethane of increased molecular weight having terminal hydroxy groups

5 (3) reacting the last-mentioned polyetherurethane with additional organic polyisocyanate to provide a polyetherurethane of further increased molecular weight having terminal isocyanate groups and (4) optionally repeating stages (2) and (3) above, the total proportion of glycol to polyisocyanate being 1 mole equivalent weight of glycol to 1.1 to 12 mole equivalent weight of organic polyisocyanate, at least 10% by weight of the total of organic polyisocyanate used being a phenylene diisocyanate and (B) reacting said prepolymer mixture with 0.5 to 5% by weight of water based on the weight of the mixture, and 0.1 to 4% by weight based on the weight of said prepolymer mixture of a polyurethane reaction catalyst in the presence of 0.25 to 5% by weight based on the weight of said prepolymer mixture of a silicone oil having a viscosity of 10 to 1,000 centistokes at 25° C. and consisting of silicon, oxygen, carbon and hydrogen atoms, to obtain a flexible cellular polyurethane reaction product.

3. A process for the production of a cellular elastic polyurethane, which comprises (A) forming a moisture-free liquid prepolymer (as herein defined) mixture by (1) reacting an organic polyisocyanate with a hydroxy terminated polyalkylene ether glycol having a molecular weight of 750 to 10,000 in an amount at least sufficient to provide a polyetherurethane having terminal hydroxy groups (2) reacting said polyetherurethane with additional organic polyisocyanate to provide a polyetherurethane of increased molecular weight having terminal isocyanate groups and, if desired, carrying out at least once the steps of (3) reacting the last-mentioned polyetherurethane with additional glycol having a molecular weight of 750 to 10,000 in an amount sufficient to provide a polyetherurethane of further increased molecular weight having terminal hydroxy groups and (4) reacting the last-mentioned polyetherurethane with additional organic polyisocyanate to provide a polyetherurethane of further increased molecular weight having terminal isocyanate groups, the total proportion of glycol to polyisocyanate being 1 mole equivalent weight of glycol to 1.1 to 12 mole equivalent weight of organic polyisocyanate, at least 10% by weight of the total of organic polyisocyanate used being a phenylene diisocyanate and (B) reacting said prepolymer mixture with 0.5 to 5% by weight of water based on the weight of the mixture, and 0.1 to 4% by weight based on the weight of said prepolymer mixture of a polyurethane reaction catalyst in the presence of 0.25 to 5% by weight based on the weight of said prepolymer mixture of a silicone oil having a viscosity of 10 to 1,000 centistokes at 25° C. and consisting of silicon, oxygen, carbon and hydrogen atoms, to obtain a flexible cellular polyurethane reaction product.

4. A process according to Claim 2 or Claim 3 characterized that in each of the stages referred to under (A) with the possible exception of the last such stage the molecular ratio of the reactants is substantially 1 to 2.

5. A process according to any one of the preceding claims, in which the phenylene diisocyanate is *para*-phenylene diisocyanate.

6. A process according to any one of Claims 1 to 4, in which the phenylene diisocyanate is *meta*-phenylene diisocyanate.

7. A process according to any one of the preceding claims, in which the phenylene diisocyanate is used in an amount of at least 20% by weight of the organic polyisocyanate.

8. A process according to the preceding claim, in which the phenylene diisocyanate is used in an amount of at least 50% by weight of the organic polyisocyanate.

9. A process according to any one of Claims 1 to 3 in which the phenylene diisocyanate is used in an amount of from 10% to 50% by weight of the organic polyisocyanate.

10. A process according to any one of the preceding claims, in which a part of the organic polyisocyanate is a mixture of 2,4- and 2,6-tolylene diisocyanates.

11. A process according to any one of the preceding claims, in which 0.5 to 1% by weight of silicone oil is used based on the weight of the prepolymer mixture.

12. A process according to any one of the preceding claims, in which the viscosity of the silicone oil is 50 to 500 centistokes at 25° C.

13. A process according to any one of the preceding claims in which the reaction catalyst is a tertiary amine.

14. A process according to any one of the preceding claims using a hydroxy terminated polyalkylene ether glycol having a molecular weight of 1500 to 5000.

15. A process according to any one of the preceding claims in which the total molecular ratio of glycol to organic polyisocyanate is 1:2 to 1:6.

16. A process according to any one of the preceding claims in which the prepolymer mixture has a viscosity of from 1500 to 100,000 cps. (Brookfield) at 25° C.

17. A process for the production of a cellular elastic polyurethane according to Claim 1 substantially as herein described.

18. A process for the production of a cellular elastic polyurethane substantially as herein described with reference to any one of Examples II to V.

19. A polyurethane foam material whenever produced by the process claimed in

any one of the preceding claims.

20. A cellular polyetherurethane elastomer having relatively fine uniform cells with a molecular chain structure comprising poly-alkylene ether residues with a molecular weight of 750 to 10,000 and organic poly-isocyanate residues, the molecular proportion of the said residues being 1:1.1 to 1:12 and at least 10% by weight of the total poly-isocyanate residues being a phenylene diisocyanate, the said elastomer also comprising 0.25 to 4% by weight of a silicone oil having

a viscosity of 10 to 1,000 centistokes at 25° C. and consisting of silicon, oxygen, carbon and hydrogen atoms.

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21. A cellular polyetherurethane elastomer produced according to the process claimed in any one of Claims 1 to 18.

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